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Kinetic Studies on the Formation of Zeolite ZSM-5

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Zeolite ZSM-5 was synthesized from sodium tetrapropylammonium aluminosilicate gels and tetrapropylammonium silicate gel. Effects of varying the ratio SiO_2/Al_2O_3 and alkalinity in the starting gels and the reaction temperature were studied. The alkalinity was found to affect the rate of nucleation more than the rate of crystal growth. An optimum alkalinity exists in the synthesis of ZSM-5; the optimum value is closely related to the value of SiO_2/Al_2O_3 ratio in the batch composition. The apparent activation energies for nucleation and crystal growth are 38 and 46 kJ mol^{-1}, respectively, for the aluminium-free silicate system and 25 and 29 kJ mol^{-1}, respectively, for the aluminosilicate system with $SiO_2/Al_2O_3 = 70$. The results are consistent with a complicated solution mechanism of crystallization.

A newly synthesized zeolite known as ZSM-5 has interesting applications in fuel and petrochemical processing.[1,2] ZSM-5 possesses a unique channel structure with an aperture of *ca.* 6 Å and an unusually high silica content.[3] These properties contribute to the excellent shape selectivity and steam and heat stability of ZSM-5.[4] This paper reports a study of the mechanism of the formation of ZSM-5. The effects of temperature and alkalinity on the syntheses were investigated by measuring the rates of nucleation and crystal growth for selected batch compositions at various temperatures. Detailed kinetic studies on the growth and A- and near-faujasite zeolites have been reported by Kerr,[5] Ciric,[6] Lechert[7] and Culfaz and Sand.[8] Some of their techniques have been followed in this work.

EXPERIMENTAL

The aluminosilicate gels were prepared from aluminium sulphate (Merck), sodium hydroxide, sulphuric acid, tetrapropylammonium bromide (TPABr) and waterglass solution (Wāko Chemical) or Ludox HS-40 colloidal silica (Du Pont).[1c] Aluminium-free silicate gel was made from 35-70 mesh silica gel (Merck) and tetrapropylammonium hydroxide (TPAOH). The TPABr was obtained from the alkylation of tripropylamine with n-propyl bromide (Aldrich). Silver oxide was refluxed with the TPABr to yield the TPAOH. The reactants were mixed homogeneously in a reaction vessel, which was sealed immediately to prevent CO_2 absorption. Synthesis runs were made at various time intervals and temperatures: above 100 °C in Teflon-lined stainless-steel autoclaves and at 100 °C or below in screw-top polypropylene bottles immersed in a water bath. After reaction, the vessel was quenched immediately in cold water and the slurry of solids was filtered, washed and dried at 110 °C.

The crystalline products were identified by X-ray powder diffraction and scanning electron microscopy, using a Jeol JSM-U3 electron microscope and a Stoe powder diffractometer with a curved graphite monochromator, controlled by a PDP-11 computer (software developed by CSS). The crystalline compounds were further examined by differential thermal analysis (d.t.a.).

The Raman spectra of the crystalline compounds were collected on a Spectra Physics 170-00 Ar^+ laser (4880 Å at *ca.* 300 mW) equipped with a Spex 1401 double-beam spectrometer (6 cm^{-1} band-pass at the sample) and a SSR photon-counting system.

Using X-ray powder diffraction (Shimadzu XD-5 X-ray diffractometer, utilizing Cu K_α radiation), the crystalline phase present in a sample was determined quantitatively by comparing the solid product with a standard end sample.[9] The extent of conversion was estimated by the formula:

$$\% \text{ conversion} = \frac{\text{peak area of } 2\theta = 22\text{-}25\,^\circ \text{ peaks of solid product}}{\text{peak area of } 2\theta = 22\text{-}25\,^\circ \text{ peaks of standard sample}}.$$

The end compounds were then converted into the ammonium form by repeated exchange with 1 mol dm^{-3} NH_4Cl solution at 80 °C. The infrared spectra of ammonium form products were obtained using the KBr wafer technique[10] on a Perkin–Elmer grating spectrophotometer 580. Gravimetric sorption determinations were carried out in a vacuum/gas handling system. The samples were pretreated by calcining at 530 °C in air for 16 h and then evacuated to 10^{-3} Torr at the same temperature. The sorptions of n-hexane and cyclohexane on samples were measured at 20 Torr and 25 °C. To study the shape-selectivity properties of NH_4ZSM-5 products, a constraint index characterization method[2a] was adopted to determine the relative cracking rates of n-hexane and 3-methylpentane on 2 cm^3 samples of 12-20 mesh size. Prior to reaction, the samples were calcined for 2 h and purged with a N_2 stream for 30 min at 530 °C. A N_2 stream containing 50/50 wt% 3-methylpentane/n-hexane was passed over the catalyst in a quartz flow reactor at 1.0 LHSV* and 1 atm. The designed conversion range for 3-methylpentane was 5-15%.

RESULT AND DISCUSSION

The crystalline end compounds and their properties are listed in table 1. All the end compounds have the same X-ray powder patterns and similar sorption and cracking properties regardless of the SiO_2/Al_2O_3 ratio in the composition. The size of crystals varied from 1 to 10 μm with the reaction mixture composition. The diffraction pattern shown in fig. 1 was recorded for a fixed time of 5 s at 0.01° intervals of the 2θ Bragg angle with Cu K_α radiation. The sample disc was rotating in a sample holder during the scan. The data were indexed to a *Pnma* orthorhombic unit cell of

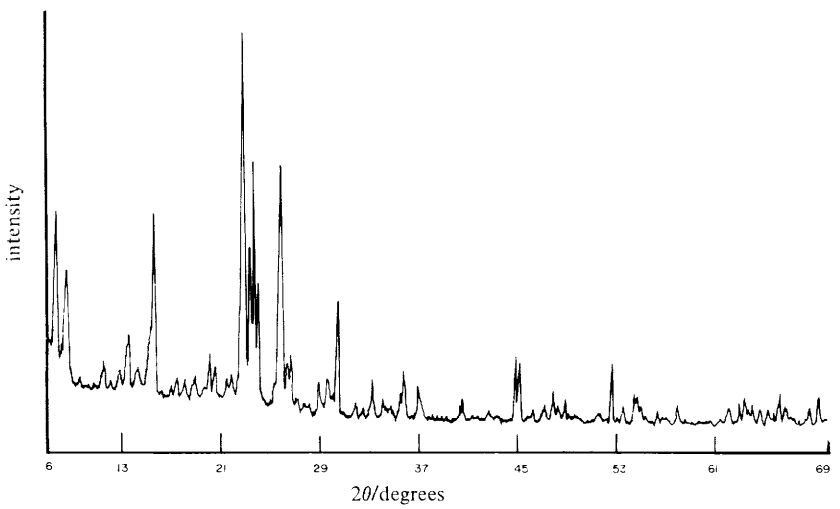

FIG. 1.—X-ray powder diffraction pattern of zeolite ZSM-5.

* LHSV = (vol. liquid feed) × (vol. catalyst h)$^{-1}$.

TABLE 1.—CRYSTALLINE PRODUCTS OBTAINED FROM THE NITROGENEOUS ALUMINOSILICATES

composition of initial mixtures[a]					zeolite ZSM-5 crystal adsorption/g g^{-1}			
SiO_2/Al_2O_3	H_2O/OH	OH/SiO_2	Na_2O/SiO_2	$(TPA)_2O$/SiO_2	Si/Al	c.i.[b]	n-C_6H_{14}	c-C_6H_{12}
70	450	0.1	0.4	0.04	30	5	0.123	0.022
90	225	0.2	0.4	0.04	35	—	—	—
	450	0.1	0.4	0.04	35	—	—	—
140	450	0.1	0.4	0.04	61	3	0.129	0.022
	225	0.2	0.4	0.04	—	—	—	—
	112	0.4	0.4	0.04	61	—	—	—
Al free	100	0.2	—	0.1	Al free	—	0.165	—

[a] SiO_2 source: silica gel for aluminium-free batch, waterglass solution for others.
[b] c.i. = $k_{\text{n-hexane}}/k_{\text{3-methylpentane}}$.

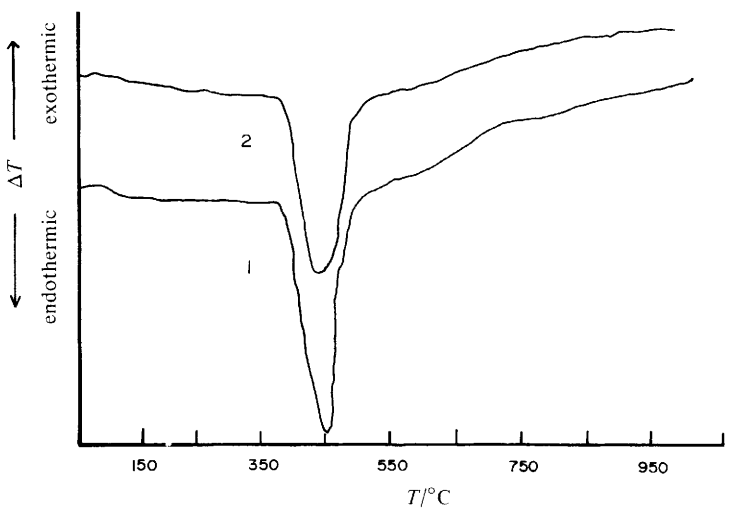

FIG. 2.—Sketch of d.t.a. curves obtained from ZSM-5 samples of SiO_2/Al_2O_3 = 122(1) and 60(2) in N_2 atmosphere. Heating rate = 30 °C min^{-1}.

dimensions a = 20.07, b = 19.92 and c = 13.42 Å. The framework of the product was found to be approximately the same as that reported by Olson.[3a] The temperature of framework decomposition is found to exceed 950 °C, as shown in fig. 2. Due to desorption of tripropylamine, the d.t.a. curves in fig. 2 also show strong endotherms at 450 °C.

The infrared spectrum of NH_4ZSM-5 is given in fig. 3. The bonding of atoms in the framework of synthetic zeolites can be interpreted in terms of the spectra in the 1300-200 cm^{-1} region.[10] Adsorption bands of external linkage were found at 545, 400, 800 and 1200-1000 cm^{-1}. In the faujasite zeolites, the bands were found at 586 or 560, 380, 782 and 1160-970 cm^{-1}. No characteristic bands were observed for double

FIG. 3.—$NH_4ZSM\text{-}5$ ($SiO_2/Al_2O_3 = 60$) infrared spectrum.

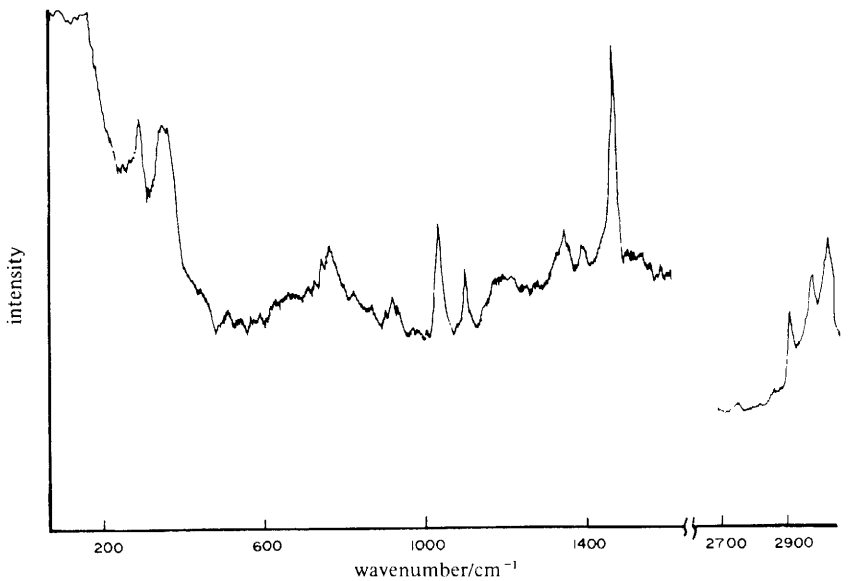

FIG. 4.—ZSM-5 ($SiO_2/Al_2O_3 = 120$) Raman spectrum.

six-membered rings at 586 and 560 cm^{-1}, nor for double four-membered rings at 650 and 500 cm^{-1}.[11] The bands at 450 and 1200-1250 cm^{-1} were assigned, respectively, to the T—O bend and the asymmetric stretch of internal tetrahedra. The absence of symmetric stretch of internal tetrahedra may be related to the particular framework structure of ZSM-5. The Raman spectrum of ZSM-5 product is given in fig. 4. As expected, the enclosed TPA ions corresponded to the adsorption bands at 1330, 1450, 2950, 3050 and 3150 cm^{-1}. The bands at 330, 350, 770, 1030 and 1090 cm^{-1} could be interpreted in terms of the vibration modes of the skeletal framework.

The framework of zeolite ZSM-5 contains a three-dimensional intersecting channels system of 10-membered rings with apertures of *ca.* 6 Å. This compares well with a diameter of 5.0 Å (Pauling width) for n-hexane, which is adsorbed, and 6.0 (Lennard-Jones kinetic diameter) or 6.7 Å (Pauling width) for cyclohexane,[12] which is adsorbed only very slightly. The sorption capacities of the end compounds are 2% by weight for cyclohexane and 12% for n-hexane, as shown in table 1. The molecular shape-selectivity of ZSM-5 is also illustrated by the relative cracking rates (c.i.) of straight chain n-hexane and the branched isomer 3-methylpentane. The c.i. values of the end compounds were 3-5, which agrees with the character of ZSM-5.[13]

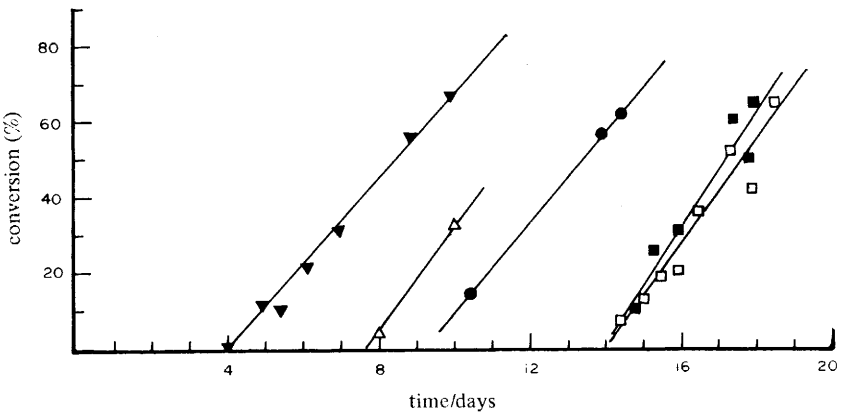

FIG. 5.—Influence of alkalinity on ZSM-5 crystallization. Temperature = 94 °C. ■, $SiO_2/Al_2O_3 = 140$, $H_2O/OH = 450$; ▼, $SiO_2/Al_2O_3 = 140$, $H_2O/OH = 225$; ●, $SiO_2/Al_2O_3 = 140$, $H_2O/OH = 112$; □, $SiO_2/Al_2O_3 = 90$, $H_2O/OH = 450$; △, $SiO_2/Al_2O_3 = 90$, $H_2O/OH = 225$.

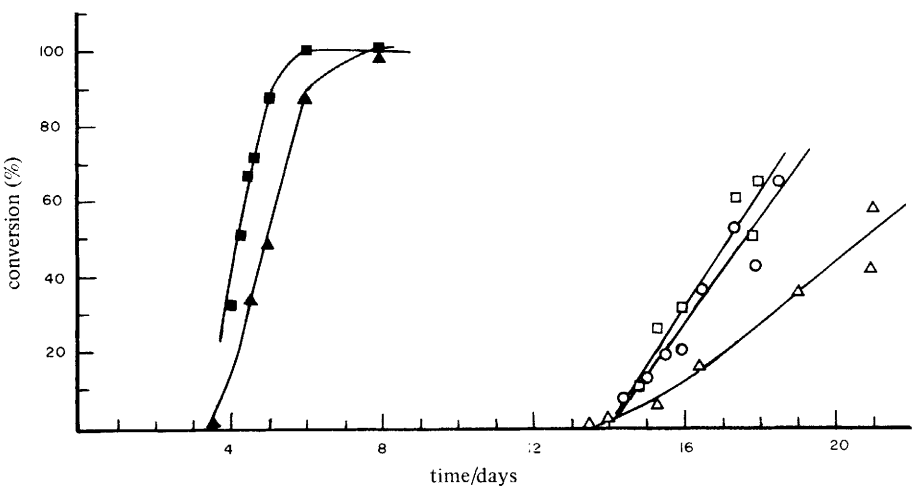

FIG. 6.—Influence of SiO_2/Al_2O_3 ratio in the batch composition on ZSM-5 crystallization at 94 and 167 °C. $H_2O/OH = 450$. □, $SiO_2/Al_2O_3 = 140$, $T = 94$ °C; ○, $SiO_2/Al_2O_3 = 90$, $T = 94$ °C; △, $SiO_2/Al_2O_3 = 70$, $T = 94$ °C; ■, $SiO_2/Al_2O_3 = 140$, $T = 167$ °C; ▲, $SiO_2/Al_2O_3 = 70$, $T = 167$ °C.

Zeolite ZSM-5 was synthesized as the crystalline phase over the temperature range 80-167 °C, as the SiO_2/Al_2O_3 ratio varied from 70 to the aluminium-free case in the batch composition. The crystallization of zeolites from hydrogels includes nucleation and crystal growth; the rate of nucleation is the reciprocal of the induction time, *i.e.* the point on a crystallization curve where conversion to the crystalline phase is just starting; the rate of crystal growth is defined as the rate of conversion at 50% of the total conversion level.[8] The crystallization curves shown in fig. 5-7 are characterized by a long induction period, followed by slow crystal growth.

As shown in fig. 5 the change in alkali concentration in the reaction mixture causes a change in the rate of nucleation and so the presence of hydroxide ions strongly affects the formation of nuclei. When solutions of the aluminate and silicate or polysilicate anions are mixed to form the hydrogels, a strong base such as NaOH or TPAOH accelerates the dissolution of the gel materials and the formation of $Al(OH)_n$. The dissolved silicate and aluminate ions can also undergo a polymerization process to aluminosilicate or polysilicate ions. The soluble aluminosilicate or polysilicate species may regroup around the hydrated cation to form the nuclei of the ordered zeolite. There exists a quasi-equilibrium between the dissolved species, the gel and the nuclei found in the liquid phase. The synthesis process may be illustrated as:

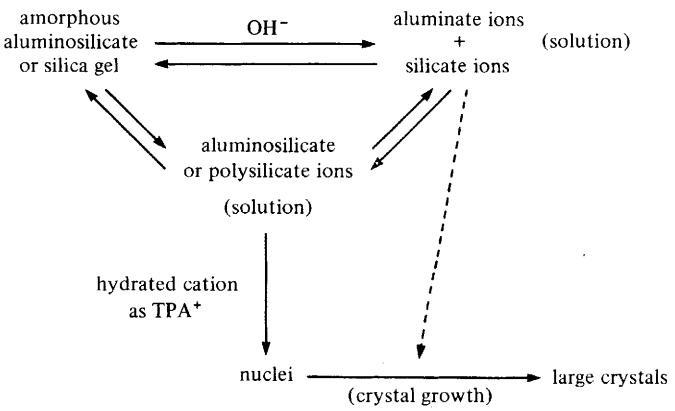

TABLE 2.—TEMPERATURE DEPENDENCE OF NUCLEATION AND CRYSTAL GROWTH

batch composition		nucleation time		activation energy/kJ mol^{-1}	
SiO_2/Al_2O_3	OH/H_2O	at 94 °C	at 167 °C	nucleation	crystal growth
Al free	1/100	42 h	3 h	38	46
140	1/450	14 d	3 d	—	—
	1/225	4 d	—	—	—
	1/112	9 d	—	—	—
90	1/450	14 d	—	—	—
	1/225	8 d	—	—	—
70	1/450	13.5 d	3.5 d	25	29

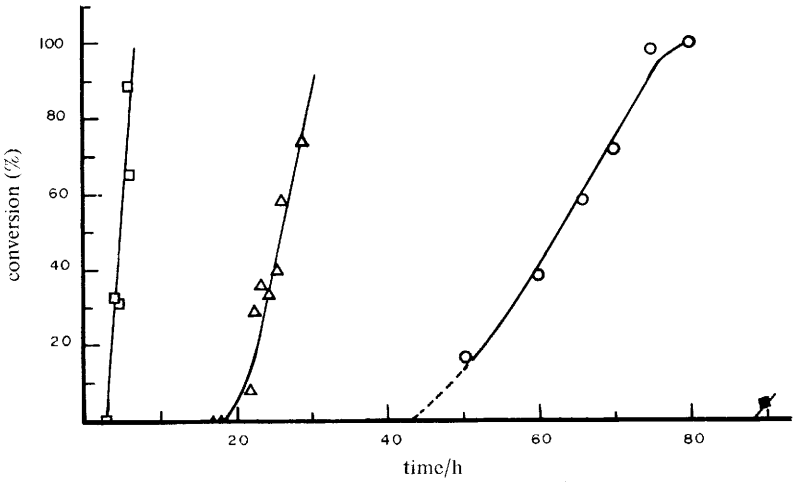

FIG. 7.—Influence of temperature on aluminium-free ZSM-5 formation. $H_2O/OH = 100$; $OH/SiO_2 = 0.2$; $(TPA)_2O/SiO_2 = 0.1$. T = ■, 80; ○, 94; △, 122; □, 167 °C.

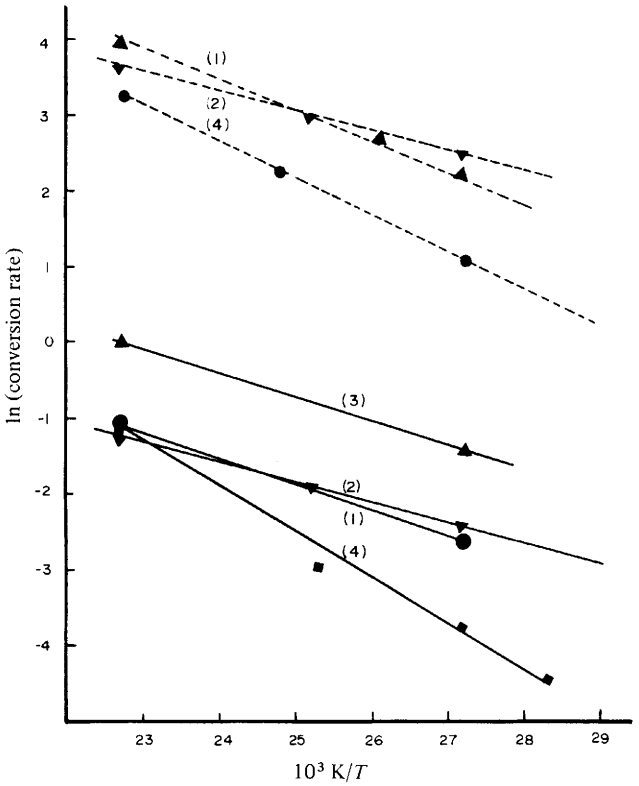

FIG. 8.—Temperature dependence of the rate of nucleation (——) and crystal growth (– – –) in (l) $SiO_2/Al_2O_3 = 140$ and $H_2O/OH = 450$, (2) $SiO_2/Al_2O_3 = 70$ and $H_2O/OH = 450$, (3) $SiO_2/Al_2O_3 = 140$ and $H_2O/OH = 225$ and (4) Al-free and $H_2O/OH = 100$ systems.

The dissolution process is accelerated by the addition of hydroxide ions which break the silicon–oxygen bonds in the gel to form small hydroxylated species. On the other hand, the polycondensation of hydroxoaluminate and silicate ions is restricted by excess hydroxide ions. Thus, an increase in hydroxide ion concentration can shorten the induction period, but higher alkalinity beyond a certain value will prolong the nucleation time. For example, in the system with $SiO_2/Al_2O_3 = 140$, the nucleation period was shortened from 14 to 4 days and then prolonged to 9 days when the OH/H_2O ratio was first increased from 1/450 to 1/225 and then increased to 1/112. This suggests the existence of an optimum alkalinity for nucleation in the synthesis of ZSM-5. Although the alkalinity strongly affects the nucleation, the crystal growth rate is almost independent of OH^- concentration, as shown in fig. 5. During the crystallization, the ionic species in the liquid phase are transported to the liquid–solid interface and then bonded to the crystals; the transportation of ionic species seems to be barely affected by the alkalinity of the solution.

Since the aluminate in the solution can form $Al(OH)_n$, which consumes OH^- ions in the solution, the available OH^- ions for depolymerization of gel probably depend on the aluminium content of the reaction mixture. Thus, the SiO_2/Al_2O_3 ratio can influence the induction period except at very low alkalinity, as shown in fig. 5. This fact also suggests that the optimum OH^- concentration may be closely related to the SiO_2/Al_2O_3 ratio of the reaction mixture. The SiO_2/Al_2O_3 ratio was also found to influence the rate of crystal growth at low alkalinity, as shown in fig. 6: the higher the SiO_2/Al_2O_3 ratio, the faster the crystal growth rate.

The apparent activation energies for the nucleation, E_n, and the crystal growth, E_c, were calculated by the Arrhenius law. The results are summarized in table 2 and fig. 8. Fig. 8 shows the independence of nucleation activation energy on the alkalinity. The E_n and E_c for the formation of aluminium-free ZSM-5 are higher than those for the other cases. The values of E_n and E_c were calculated to be 25 and 29 kJ mol^{-1}, respectively, for $SiO_2/Al_2O_3 = 70$ and $OH/H_2O = 1/450$ and 38 and 46 kJ mol^{-1},

TABLE 3.—INFLUENCE OF TPA ION CONCENTRATION AND THE SILICA SOURCE ON ZEOLITE ZSM-5 CRYSTALLIZATION

composition in initial mixtures						reaction conditions		ZSM-5 crystallini
SiO_2 source	SiO_2/Al_2O_3	H_2O/OH	OH/SiO_2	Na_2O/SiO_2	$(TPA)_2O/SiO_2$	temp./°C	time	(%)
silica gel	Al free	100	0.2	0.1	0	94	50 h	0
	Al free	100	0.2	0.06	0.04	94	72 h	2
	Al free	100	0.2	0	0.1	94	50 h	16
sodium silicate	140	450	0.1	0.4	0	167	8 d	26[a]
	140	450	0.1	0.4	0.04	167	7 d	100
	140	225	0.2	0.4	0	124	7 d	0
	140	225	0.2	0.4	0.04	124	5 d	100
	140	225	0.2	0.4	0.04	94	6 d	21
colloidal silica	140	225	0.2	0.4	0.04	94	6 d	59
	140	225	0.2	0.4	0.04	94	8 d	69
silica gel	140	225	0.2	0.4	0.04	94	7.5 d	14
	140	225	0.2	0.4	0.04	94	8.5 d	16

[a] ZSM-5 + other crystalline phase.

respectively, for the aluminium-free silicate gel. To reach the same OH/SiO_2 ratio, the reaction batch contained a higher TPA concentration for the aluminium-free silicate gel prepared from TPAOH and silica gel than that for the aluminosilicate gels prepared from TPABr, NaOH, $Al_2(SO_4)_3$ and sodium silicate. As a result, the rate of conversion of $TPAOH–10SiO_2–100H_2O$ was found to very fast and ZSM-5 was formed in a few hours at 167 °C. The strong influence of TPA ions on the formation of ZSM-5 is shown in table 3; an increase in the $(TPA)_2O/SiO_2$ ratio raises the rate of conversion. It was also observed that ZSM-5 could be formed with TPA^+ as the only cation in the reaction mixture. The TPA ions, acting as the template, attract the building units to form the nuclei and to stabilize the framework structure of ZSM-5. However, the alkalinity of the reaction mixture is affected by TPA^+ concentration since TPA^+ ions may combine with OH^- ions to form TPAOH. In addition, the SiO_2 source also affects the rate of ZSM-5 formation. The relative rate of conversion to ZSM-5 increases in the order: silica gel < sodium silicate < colloidal silica, as shown in table 3.

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